AD-A241 333



320

REPORT	DOCUMENTATIO	N PAGE		W-30-7-		Approved Vo. 0704-0188
la REPORT SECURITY CLASSIFICATION Unclassified		16. RESTRICTIVE	MARKINGS		<u>-</u>	
2a SECURITY CLASSIF CATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approval for public release; distribution unlimited				
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE						
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. DU/DC/TR-24		5. MONITORING ORGANIZATION REPORT NUMBER(S)				
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Duke University	6b. OFFICE SYMBOL (If applicable)					
6c. ADDRESS (City, State, and ZIP Code) Durham, NC 27706		7b. ADDRESS (City, State, and ZIP Code) 300 North Quincy Street Arlington, VA 22217-5000				
8a. NAME OF FUNDING, SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER NOO014-89-J-1545; R&T Code 4135008				
8c. ADDRESS (City, State, and ZIP Code)	<u> </u>	10. SOURCE OF F				
800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO. NR	PROJECT NO. 053	TASK NO. 84	41	WORK UNIT ACCESSION NO.
11 TIFLE (include Security Classification) ON THE SYNTHESIS AND CHARACT STRUCTURE OF [Et2AlAs(SiMe3)2]2 12 PERSONAL AUTHOR(S)	TERIZATION OF NO	VEL ALUMINUN	1-ARSENIC CO	MPOUN	DS; CR	YSTAL
Wells, A.T. McPhail, and	T. M. Speer					
		14. DATE OF REPO 1991-10-03	RT (Year, Month, I	Oay) 15	. P AGE C 18	
16 SUPPLEMENTARY NOTATION Accepted for publication in C	rganometallics					
17 COSATI CODES	18. SUBJECT TERMS	Continue on reverse	e if necessary and	identity	by block	number)
FIELD GROUP SUB-GROUP	alumium-arsenic, syn		synthesis, crystal structure,			
ring compound 19 ABSTRACT (Continue on reverse if necessary and identify by block number)						
See attached.	and roentry by block i	umo e r)	91-1	270 	6	
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT		21. ABSTRACT SE	CURITY CLASSIFICA		e () (7 %
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS I	RPT TOTIC USERS	Unclassifi				

■ UNCLASSIFIED/UNLIMITED ■ SAME AS RPT

Richard L. Wells

TOTIC USERS

22b. TELEPHONE (Include Area Code) | 22c OFFICE SYMBOL

(919)660-1541

(ALPEARSO

[19. ABSTRACT]]

On the Synthesis and Characterization of Novel
Aluminum-Arsenic Compounds;
Crystal Structure of [Et2AlAs(SiMe3)2]2.

Acesasion for NTIN GRANI Bric Tab Universal world Justification

TENNONIOUTIUS DE AM®114kts se ELLE AMMILIER Disterresses

A-1

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

Department of Chemistry, Paul M. Gross Chemical Laboratory

Duke University, Durham NC, 27706

(Received, 1991)

ABSTRACT

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type AI-As-AI-As and AI-As-AI-CI was investigated. The second fully characterized aluminum-arsenic dimer, $[Et_2AIAs(SiMe_3)_2]_2$ (1), was isolated from a coupling reaction between Et_2AICI and $LiAs(SiMe_3)_3$ carried out at -78 °C. Dehalosilylation reactions between Et_2AICI and $As(SiMe_3)_3$ in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected products, instead yielding the adduct $Et_2(CI)AI-As(SiMe_3)_3$ (2). As evidenced by ¹H NMR spectra, an NMR tube sample of ² in benzene-d6 did undergo internal dehalosilylation to give 1 when heated to 87 °C in an oil bath. X-ray crystallographic analysis of 1 confirms its dimeric solid-state structure and shows the AI-As-AI-As ring to be planar. Compound 1 crystallizes in the monoclinic system, space group C2/c ($C2h^6$), with four molecules in a unit cell of dimensions: a = 18.214(2) Å, b = 9.542(1) Å, c = 20.453(2) Å, $\beta = 99.89(1)^\circ$.

OFFICE OF NAVAL RESEARCH

Grant NOOO14-89-J-1545

R&T Code 4135008

Technical Report No. DU/DC/TR-24

ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC COMPOUNDS; CRYSTAL STRUCTURE OF [Et₂AlAs(SiMe₃)₂]₂

by

R. L. Wells, A. T. McPhail, and T. M. Speer

Prepared for Publication in Organometallics

Duke University
Department of Chemistry
Durham, NC 27706

October 3, 1991

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

On the Synthesis and Characterization of Novel Aluminum-Arsenic Compounds; Crystal Structure of [Et₂AIAs(SiMe₃)₂]₂.

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

Department of Chemistry, Paul M. Gross Chemical Laboratory

Duke University, Durham NC, 27706

(Received, 1991)

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type Al-As-Al-As and Al-As-Al-Cl was investigated. The second fully characterized aluminum-arsenic dimer [Et₂AlAs(SiMe₃)₂]₂ (1), was isolated from a coupling reaction between Et₂AlCl and LiAs(SiMe₃)₃ carried out at -78 °C. Reactions between Et₂AlCl and As(SiMe₃)₃ in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected dehalosilylation products, instead yielding the adduct Et₂(Cl)Al•As(SiMe₃)₃ (2). As evidenced by ¹H NMR spectra, an NMR tube sample of 2 in benzene-d6 did undergo internal dehalosilylation to give 1 when heated to 87 °C in an oil bath. X-ray crystallographic analysis of 1 confirms its dimeric solid-state structure and shows the Al-As-Al-As ring to be planar. Compound 1 crystallizes in the monoclinic system, space group C2/c (C_{2h}^{6}), with four molecules in a unit cell of dimensions: a = 18.214(2) Å, b = 9.542(1) Å, c = 20.453(2) Å, $b = 99.89(1)^\circ$.

INTRODUCTION

Of late, there has been heightened interest in the preparation of compounds that may serve as single-source precursors to Group 13-15 semiconductor materials. 1.2 Two methods have been developed in our laboratories to fabricate compounds that may prove useful to this end: a) dehalosilylation between tris(trimethylsilyl)arsine and a Group 13 halide and b) coupling reactions involving lithium bis(trimethylsilyl)arsenide and a Group 13 halide. These methodologies have been applied to systems involving the heavier Group 13 elements to prepare compounds with core rings of the type $\overline{\text{M-As-M-As}}$ and $\overline{\text{M-As-M-Cl}}$, where $\overline{\text{M}} = Ga$ and $\overline{\text{In.}^{3-7}}$ In an attempt to utilize these tactics to prepare analogous aluminum-arsenic species, reaction of $\overline{\text{Et}_2} \overline{\text{AlCl}}$ with $\overline{\text{tris}}(\overline{\text{trimethylsilyl}}) \overline{\text{arsine}}$ and $\overline{\text{lithium}}$ bis(trimethylsilyl)arsenide was undertaken. While proving useful in the cases of Ga and In, room temperature dehalosilylation reactions failed in this work instead yielding the adduct $\overline{\text{Et}_2}(Cl)\overline{\text{Al-As}}(SiMe_3)_3$ (2). The novel dimer $[\overline{\text{Et}_2}\overline{\text{AlAs}}(SiMe_3)_2]_2$ (1), was prepared by a coupling reaction and is only the second Al-As dimer fully characterized by single crystal X-ray analysis.

EXPERIMENTAL

General Considerations. All reactions and manipulations were carried out utilizing standard Schlenk techniques, under an Ar atmosphere in a Vacuum/Atmospheres HE-43 Dri-Lab or under vacuum. Pentane and hexane were dried over LiAlH₄ while all other solvents were dried over, and distilled from, sodium benzophenone ketyl. Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide

were prepared by the methods of Becker *et al.*⁸ Diethylaluminum chloride was purchased from Strem Chemicals, Inc. and used without further purification. ¹H, ¹³C{¹H} and ²⁷Al{¹H} NMR spectra were obtained at 299.943, 75.4 and 78.2 MHz, respectively, on a Varian XL-300 spectrometer in 5 mm tubes. ¹³C{¹H} and ¹H NMR spectra were referenced to TMS using the carbons or residual protons of benzene-d₆ at δ 128 ppm and δ 7.15 ppm, respectively. ²⁷Al{¹H} spectra were referenced externally to Al(NO₃)₃ at δ 0.00 ppm. All spectra were run in benzene-d₆ and NMR tubes were flame sealed under vacuum. Melting points were obtained on a Hoover Uni-Melt in sealed capillaries and are uncorrected. Elemental anlyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Crystals used in X-ray analyses were flame sealed under argon in 0.7 mm thin-walled glass capillaries. Volatile reaction products were analyzed for Me₃SiCl content by hydrolysis with deionized water followed by titration of the resulting HCl solution with standard NaOH to a phenolphthalein endpoint. NaOH was standardized against potassium hydrogen phthalate to a phenolphthalein endpoint.

Preparation of [Et₂AlAs(SiMe₃)₂]₂ (1). LiAs(SiMe₃)₂ (0.373 g, 1.63 mmol) was dissolved in 25 mL of pentane and 10 mL of THF in the top bulb of a two-bulb reaction flask. Et₂AlCl (0.1969 g, 1.633 mmol) was washed into the bottom bulb with 35 mL pentane. The lower bulb was cooled to -78 °C in an acetone/dry ice bath and the upper bulb was cooled with a liquid nitrogen wand. Upon mixing, a white precipitate formed (presumably LiCl, 0.0588 g, 87% yield) and the solution remained clear. After stirring for 18 h at -78 °C, the reaction mixture was allowed to warm slowly to room temperature and volatiles were removed *in vacuo* to leave an off-white semi-solid that was recrystallized at -15 °C from pentane to give 1 (0.651 g, 65.2% yield), mp 201 °C. No Me₃SiCl was eliminated over the course of the reaction. Anal. Calcd. (found) for C₂₀H₅₆Al₂As₂Si₄: C 39.20 (39.40), H 9.15 (9.16). ¹H NMR: δ 0.42

[s, Si(C H_3)₃, 18H], 0.51 (q, C H_2 , 4H) 1.38 (t, C H_3 . 6H). ¹³C{¹H} NMR: δ 4.65 [s, Si(C H_3)₃], 9.68 (s, C H_3), CH₂ not observed. ²⁷Al{¹H} NMR: δ 181.87 (br s).

Preparation of Et₂(Cl)Al·As(SiMe₃)₃ (2). (a) Reaction of Et₂AlCl with As(SiMe₃)₃ (1:1 mole ratio). Et₂AICI (0.2058 g. 1.670 mmol) in 25 mL of pentane was added to As(SiMe₃)₃ (0.492 g, 1.67 mmol) in 25 mL of pentane in a onenecked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was noted upon mixing. Following stirring at room temperature for 3 d, volatiles were removed in vacuo leaving an off-white solid that was recrystallized from pentane at -15 °C to give 2 (0.684 g, 98.7% yield), mp 138 °C. No Me₃SiCl was eliminated over the course of the reaction. Anal. Calcd. (Found) for C₁₃H₃₇AlAsClSi₃: C 37.62 (37.37), H 8.99 (8.89), Cl 8.54 (8.12). ¹H NMR: δ 0.28 [s, Si(C H_3)₃, 27 H], 0.46 (q, C H_2 , 4H), 1.52 (t, C H_3 , 6H). ¹³C{¹H} NMR: δ 3.09 (s, Si(CH₃)₃), 9.77 (s, CH₃), CH₂ not observed. ²⁷Al{¹H} NMR: δ 165.32 (br s). (b) Reaction of Et₂AlCl with As(SiMe₃)₃ (2:1 mole ratio). Et₂AlCl (0.3934 g, 3.20 mmol) in 20 mL pentane was added to As(SiMe₃)₃ (0.470 g, 1.60 mmol) in 30 mL pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was seen upon addition. Following stirring for 3 d at room temperature, volatiles were removed in vacuo to leave an off-white solid which was recrystallized from pentane at -15 °C to give clear crystals (0.653 g 98.3% yield), mp and NMR spectra (¹H and ¹³C{¹H}) match those of an authentic sample of 2, vide supra. No Me₃SiCl was eliminated over the course of the reaction.

Intramolecular Dehalosilylation of 2 to Form 1. An NMR tube sample of 2 in benzene-d₆ was heated to 87 °C in an oil bath for 4 d. ¹H NMR spectra taken over this time showed peaks consistent with an authentic sample of 1 and one that may be attributed to Me₃SiCl at δ 0.165, indicating that internal dehalosilylation occurred.

Attempted Conversion of 1 to Et₂AIAs(SiMe₃)₂AI(Et)₂CI. Et₂AICI (0.0376 g, 0.312 mmol) in 20 mL of pentane was added to 1 (0.0956 g, 0.156 mmol) in a one-necked, round-bottomed flask fitted with a Teflon valve and equipped with a magnetic stir bar. Following stirring for 2 d at room temperature, volatiles were removed *in vacuo* to leave an off white semi-solid that was recrystallized from pentane at -15 °C, mp and NMR spectra (Its ¹H and ¹³C{¹H}) matched those of an authentic sample of 1, *vide supra*, indicating no reaction had occurred.

X-Ray Crystal Structure Analysis of 1. Crystallographic data are summarized in Table I. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the φ-dependency of the intensities of several reflections with ψ ca. 90°, was also applied. The crystal structure was solved by the heavy-atom approach. The systematically absent reflections: hkl when $h + k \neq 2n$ and h0l when $l \neq 2n$, are compatible with two space groups, viz. Cc and C2/c. With only four formula units in the latter, dimeric moleules must either lie on a crystallographic center of symmetry or C_2 symmetry axis. Approximate coordinates for the As atoms, derived from a Patterson map, were related by a center of symmetry and thus all further calculations were performed using equivalent positions appropriate to the centrosymmetric space group C2/c. The remaining non-hydrogen atoms were located in a series of weighted F_0 and difference Fourier syntheses. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) and an extinction correction was included as a variable. A final difference Fourier synthesis contained no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 9.

DISCUSSION

$$nEt2AlCl + As(SiMe3)3 \longrightarrow Et2(Cl)Al•As(SiMe3)3 + (n-1)Et2AlCl$$

$$n = 1,2$$
(1)

This behavior may be understood by consideration of the relative strengths of the Group 13-Cl bonds. They are 420.7, 354.0 and 328.0 kJmol⁻¹ for Al, Ga and In, respectively.¹⁰ Since this bond is much stronger in the case of aluminum, its cleavage may be energetically unfavored and, hence, dehalosilylation is not observed. Instead, simple adducts are formed. To date, reaction conditions have not been varied to elucidate the effect of temperature upon such reactions. Such steps may provide a driving force that would enable dehalosilylation to occur.

While crystals of 2 suitable for single crystal X-ray analysis have not been obtained, other data support the postulation of its structure as an adduct. Its ¹H,

¹³C{¹H} and ²⁷Al{¹H} NMR spectra suggest such a formulation in that the ¹H integration and splitting patterns are compliant, the ¹³C{¹H} spectrum intensities are appropriate for those peaks observed and only one type of aluminum is present as evidenced by a single peak in the ²⁷Al{¹H} spectrum. This, coupled with a partial elemental analysis (C, H and Cl), the fact that no Me₃SiCl was found in reaction volatiles and that yield was nearly quantitative, indicates that the structure of the product is correctly stated as 2.

It was previously shown by us that the adduct Cl₃Al•As(SiMe₃)₃ undergoes intramolecular dehalosilylation to give AlAs when heated neat, under vacuum, in a cool flame.¹¹ With this in mind, attempted internal dehalosilylation of **2** was undertaken. Here, however, it was achieved at a much lower temperature. An NMR tube sample of **2** in benzene-d₆ was heated at 87 °C for four days. ¹H NMR spectra taken as early as one day after heating showed peaks that may be attributed to compound **1** and Me₃SiCl. Thus, dehalosilylation may be brought about under very mild conditions in the case of **2** (eq 2).

$$2Et2(Cl)A! \cdot As(SiMe3)3 \longrightarrow [Et2AlAs(SiMe3)2]2 + 2Me3SiCl$$
 (2)

Compound 1 was prepared initially in relatively high yield (65%) by employing a coupling reaction between LiAs(SiMe₃)₂ and Et₂AlCl at -78 °C (eq 3). When carried

$$2Et_2AlCl + 2LiAs(SiMe_3)_2 \longrightarrow [Et_2AlAs(SiMe_3)_2]_2 + 2LiCl$$
 (3)

out at room temperature, product was obtained in very low yield with an uncharacterized viscous, orange liquid as the predominant product. It is noteworthy

that, prior to this work, only four other arsinoalanes had ever been reported.¹²⁻¹⁵ Three of them are dimess^{12,14,15}, but only one was fully characterized by single crystal X-ray analysis¹⁵

The conversion of sundry Group 13-As dimers to mixed-bridge compounds by treatment with two mole equivalents of a dialkyl Group 13 halide has been shown to be applicable to such Ga and In containing species.^{5,16,17} However, it was found that this methodology was not successful for 1. Upon treatment with two mole equivalents of Et₂AlCl, no reaction was observed (eq 4), as evidenced by ¹H and ¹³C NMR spectra.

This suggests that perhaps the dimer does not undergo dissociation in solution, thus not allowing for the monomeric unit to react with the aluminum halide.

Crystals of 1 suitable for X-ray analysis were grown from pentane. Crystallographic data are reported in Table I. An ORTEP diagram showing the atom numbering scheme is presented in Figure I. Table II lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters while selected bond lengths and angles are given in Table III.

Compound 1 crystallizes in the monoclinic space group C2/c with the four discrete dimeric molecules in the unit cell lying on crystallographic centers of symmetry, and thus the Al-As-Al-As ring is constrained to be exactly planar as is the case for the only other previously characterized aluminum-arsenic dimer, $[Et_2AlAs(t-Bu)_2]_2$ (3).¹⁵ The mean Al-As distance of 2.535 Å in 1 is slightly shorter that that of 2.567 Å in 3. The mean of the Al-C(1) [1.965(6) Å] and Al-C(3) [1.986(6) Å] bond distances at 1.976 Å in 1 is also slightly less than the corresponding mean of 1.992 Å in 3. The geometry

about the AI and As atoms in 1 is distorted tetrahedral with the endocyclic angle subtended at As [AI-As-AI' = $91.01(5)^{\circ}$] being slightly larger than that at AI [As-AI-As' = $88.99(5)^{\circ}$]; the difference between the AI-As-AI' and As-AI-As' angles in 3 [$94.54(4)^{\circ}$ vs. $85.64(4)^{\circ}$] is much more pronounced. The Si-As-Si and C-AI-C angles at $107.59(6)^{\circ}$ and $115.0(3)^{\circ}$ in 1 deviate from tetrahedral in the same sense as do the C-As-C and C-AI-C angles, $108.9(3)^{\circ}$ and $111.5(3)^{\circ}$, respectively, in 3.

Compound 1 is of particular interest because it may be useful as a single-source precursor for the facile formation of AlAs. There are several ways in which this molecule may be envisaged as being utilized for such purposes. The ethyl groups provide for the possibility of β-hydrogen transfer with concurrent evolution of ethene and subsequent elimination of trimethylsilane to give AlAs. A second possibility is alcoholysis. Douglas and Theopold showed that a Ga-As dimer, when treated with methanol, underwent internal elimination to give GaAs.¹⁸ The third way in which AlAs might be obtained is to take advantage of the fact that covalent halides are known to cleave the silicon-arsenic bond.¹⁹ Thus, treatment of 1 with HCl should afford Me₃SiCl and an AsH₂-containing species which should readily eliminate ethane, or ethene and dihydrogen, to yield AlAs.

CONCLUSIONS

The work presented herein shows the viability of lithium chloride elimination reactions in the preparation of aluminum-arsenic dimers. While this methodology was successfully applied, dehalosilylation reactions were ineffective in that an aluminum-arsenic-chlorine mixed-bridge compound nor a dimer could be prepared directly by this route; albeit, evidence was obtained which indicated an adduct underwent dehalosilyation on heating to give a dimer. This study will be used as a starting point for further investigation of aluminum-arsenic systems. Through variation of temperature, substituents on aluminum and other reaction conditions a better

understanding of the limitations and applications of lithium halide elimination and dehalosilylation reactions to the preparation of single-source precursors to AlAs may be developed.

Acknowledgements. Financial support from the Office of Naval Research is greatly appreciated.

Supplementary Materials Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete lists of interatomic distances and angles, including torsion angles for 1, and equations of least-squares planes through groups of atoms (5 pages); a listing of observed and calculated structure amplitudes for 1 (14 pages). Ordering information is given on any current masthead page.

References

- (1) Cowley, A.H.; Jones, R.A. Angew. Chem. Intl. Ed. Engl. 1989, 28, 1208.
- (2) Cole-Hamilton, D.J. Chem. in Brit. 1991, 852.
- (3) Purdy, A.P.; Wells, R.L.; McPhail, A.T.; Pitt, C.G. Organometallics 1987, 6, 2099.
- (4) Holley, W.K.; Pasterczyk, J.W.; Pitt, C.G.; Wells. R.L. *Heteroatom Chem.* **1990**, 1, 475.
- (5) Wells, R.L.; Jones, L.J.; McPhail, A.T.; Alvanipour, A. *Organometallics*. **1991**, *10*, 2345.
- (6) Wells, R.L.; Purdy, A.P.; Higa, K.T.; McPhail, A.T.; Pitt, C.G. J. Organomet. Chem. 1987, 325, C7.
- (7) Wells, R.L.; Holley, W.K.; Shafieezad, S.; McPhail, A.T., Pitt, C.G. *Phosphorus, Sulfur, Silicon and Related Elem.* **1989**, *41*, 15.
- (8) Becker, G.; Gutekunst, G.; Wessely, H.J., Z. Anorg. Allg. Chem 1980, 462, 113.
- (9) International Tables for X-ray Crystallography, The Kynoch Press, Birmingham, England, 1974, Voi IV.
- (10) Huheey, J.E. *Inorganic Chem. 3rd Ed.* Harper and Row Publishers, New York, NY, 1983.
- (11) Wells, R.L.; Pitt, C.G.; McPhail, A.T.; Purdy, A.P.; Shafieezad, S.; Hallock, R.B. Mat. Res. Soc. Symp. Proc. 1989, 131, 45.
- (12) Coates, G.E.; Graham, J. J. Chem. Soc. 1963, 233.
- (13) Beachley, O.T.; Coates, G.E. J. Chem. Soc. 1965, 3241.
- (14) Arif, A.M.; Benac, B.L.; Cowley, A.H.; Jones, R.A.; Kidd, K.B.; Nunn, C.M. New J, Chem.1988, 12, 253.
- (15) Heaton, D.E.; Jones, R.A.; Kidd, K.B.; Cowley, A.H.; Nunn, C.M. *Polyhedron* **1988**, 7, 1901.

- (16) Holley, W.K.; Wells, R.L.; Shafieezad, S.; McPhail, A.T.; Pitt, C.G. *J. Organomet. Chem.* **1990**, *381*, 15.
- (17) Wells, R.L.; Pasterczyk, J.W.; McPhail, A.T.; Johansen, J.D.; Alvanipour, A. *J. Organomet. Chem.* **1991**, *407*, 17.
- (18) Douglas, T.; Theopold, K.H. Inorg. Chem. 1991, 30, 596.
- (19) Abel, E.W.; Illingworth, S.M. J. Chem. Soc. (A) 1969, 1094.

Caption to Figure

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the solid-state conformation and atom numbering scheme of [Et₂AlAs(SiMe₃)₂]₂ (1); primed atoms are related to unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

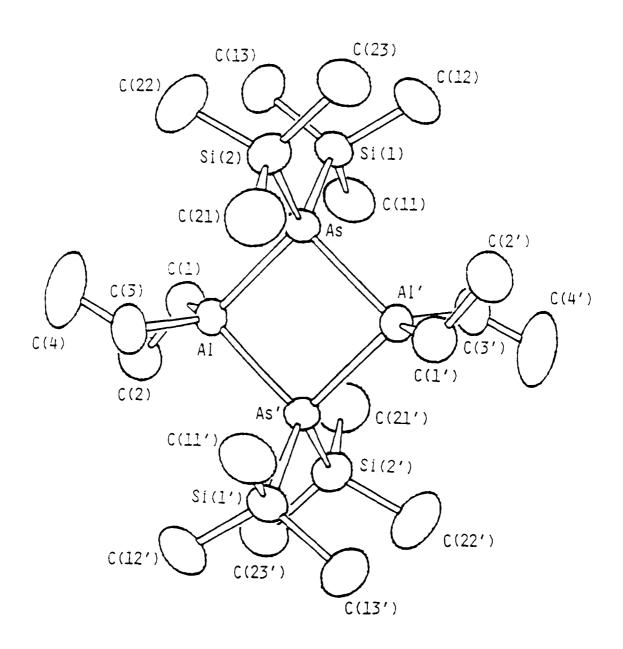


Table 1. Crystallographic Data^a for [Et₂AlAs(SiMe₃)₂]₂ (1)

	0 11 11 1 0
Molecular formula	C ₂₀ H ₅₆ Al ₂ As ₂ Si ₄
Formula weight	612.82
Crystal system	monoclinic
Space group	$C2/a(C_{2h}^{6})$ - No.15
a(Å)	18.214(2)
b(Å)	9.542(1)
c(Å)	20.453(2)
β(°)	99.89(1)
No. of orientation refls.; θ(°) range	25; 40-45
V(ų)	3502(1)
Z	4
D _{calcd.} (g cm ⁻³)	1.162
μ (Cu- $K\alpha$ radiation, I = 1.5418 Å)	42.5
Temp. (°C)	23
Crystal dimensions (mm)	$0.15 \times 0.25 \times 0.32$
T _{max} :T _{min}	1.00:0.65
Scan type	ω-2θ
Scanwidth (°)	$0.70 + 0.14 \tan \theta$
θ _{max.} (°)	75
Intensity control refls.;	312,222,131,224;
variation; repeat time (hr)	<2%;2
Total no. of refls. $(+h,+k,\pm l)$ recorded	3705
No. of non-equiv. refls. recorded	3118
R _{merge} (on 1)	0.023
No. of refls. retained $[/>3.0\sigma(/)]$	1968
No. of parameters refined	128
Extinction correction	3.7(1) x 10 ⁻⁶
$R(R_{w})^{b}$	0.039 (0.053)
Goodness-of-fit ^C	1.11
Max. shift:esd in final least-squares cycle	0.02
Final Δρ(e/ų) max.;min.	0.32 ; -0.58
• •	

^aAn Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochrometer was used for all measurements. Crystallographic calculations were performed on PDP11/4

Table 1. (Continued)

and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP).

 $bR = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$; $R_W = [\Sigma \omega (|F_0| - |F_c|)^2/\Sigma \omega |F_0|^2]^{1/2}$; $\Sigma \omega D^2 [\omega = 1/\sigma^2 (|F_0|), \Delta = (|F_0| - |F_c|)]$ was minimized.

^QGoodness-of-fit = $[\Sigma \omega \Delta^2/(N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

Table II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

Atom	X	y	Z	$B_{eq}(Å^2)$
As	0.18753(3)	0.25453(6)	-0.07961(2)	4.06(1)
Al	0.18075(7)	0.3337(2)	0.04040(7)	4.25(3)
Si(1)	0.10419(8)	0.0731(2)	-0.11613(7)	5.27(3)
Si(2)	0.17122(9)	0.4338(2)	-0.15669(7)	5.68(3)
C(1)	0.1045(3)	0.2321(6)	0.0788(3)	5.7(1)
C(2)	0.1042(4)	0.2663(7)	0.1520(3)	7.5(2)
C(3)	0.1774(3)	0.5409(6)	0.0486(3)	6.7(1)
C(4)	0.1042(4)	0.6022(8)	0.0471(5)	11.8(2)
C(11)	0.1094(4)	-0.0631(7)	-0.0520(3)	7.8(2)
C(12)	0.0072(3)	0.1409(8)	-0.1347(4)	9.4(2)
C(13)	0.1301(4)	-0.0092(8)	-0.1915(3)	8.2(2)
C(21)	0.0790(4)	0.5213(9)	-0.1594(4)	10.0(2)
C(22)	0.1754(4)	0.3628(9)	-0.2401(3)	8.3(2)
C(23)	0.2467(4)	0.5662(7)	-0.1334(4)	8.8(2)

Table III. Selected Bond Distances (Å) and Angles (deg) for 1 with Estimated Standard Deviations in Parentheses

Bond Lengths

C(3)-Al-As' 110.3(2)

As-Al As-Si(2) Al-C(1)	2.539(2) 2.347(2) 1.965(6)	As-Si(1) As-Al' Al-C(3)	2.351(2) 2.531(1) 1.986(6)		
Bond Angles					
Al-As-Si(1)	114.10(6)	Al-As-Si(2)	114.79(6)		
Al-As-Al'	91.01(5)	Si(1)-As-Si(2)	107.59(6)		
Si(1)-As-Al'	112.30(6)	Si(2)-As-Al'	116.60(6)		
As-Al-C(1)	112.5(2)	As-Al-C(3)	112.5(2)		
As-Al-As'	88.99(5)	C(1)-AI-C(3)	115.0(3)		

C(i)-Al-As 114.7(2)

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Christon, Code 1113
800 North Quincy Street
Arlington, VA 22217-5000

Dr. James S. Murday (1) Chemistry Division, Code 6100 Naval Research Laboratory Washington, DC 20375-5000

Dr. Robert Green, Director (1) Chemistry Division, Code 385 Naval Weapons Center China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1) Code 2840 David Taylor Research Center Annapolis, MD 21402-5067

Dr. Elek Lindner (1) Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000 Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, IN 47522-5050

Dr. Richard W. Drisko (1) Naval Civil Engineering Lab. Code L52 Port Hueneme, CA 93043

Dr. Harold H. Singerman (1) David Taylor Research Center Code 283 Annapolis, MD 21402-5067

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical Information Center (2) Building 5, Cameron Station Alexandria, VA 22314